

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
24 July 2003 (24.07.2003)

PCT

(10) International Publication Number  
**WO 03/060980 A2**

(51) International Patent Classification<sup>7</sup>: **H01L 21/321**

(21) International Application Number: PCT/US02/40407

(22) International Filing Date:  
17 December 2002 (17.12.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
10/032,357 21 December 2001 (21.12.2001) US

(71) Applicant: **MICRON TECHNOLOGY, INC.** [US/US];  
8000 South Federal Way, Boise, ID 83704-0006 (US).

(72) Inventors: **UHLENBROCK, Stefan**; 11336 W. Divide  
Pass Dr., Boise, ID 83709 (US). **WESTMORELAND,  
Donald, L.**; 10258 West Alliance Street, Boise, ID 83704  
(US).

(74) Agent: **MUETING, Ann, M.**; Mueting, Raasch & Geb-  
hardt, P.A., P.O. Box 581415, Minneapolis, MN 55458-  
1415 (US).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,  
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,  
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,  
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,  
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,  
MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG,  
SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VN, YU,  
ZA, ZM, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM,  
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),  
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),  
European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE,  
ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SI, SK,  
TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ,  
GW, ML, MR, NE, SN, TD, TG).

**Published:**

— *without international search report and to be republished  
upon receipt of that report*

*For two-letter codes and other abbreviations, refer to the "Guid-  
ance Notes on Codes and Abbreviations" appearing at the begin-  
ning of each regular issue of the PCT Gazette.*



**WO 03/060980 A2**

(54) Title: **METHODS FOR PLANARIZATION OF GROUP VIII METAL-CONTAINING SURFACES USING OXIDIZING GASES**

(57) Abstract: A planarization method includes providing a second and/or third Group VIII metal-containing surface (preferably, a platinum-containing surface) and positioning it for contact with a polishing surface in the presence of a planarization composition that includes an oxidizing gas.

**BEST AVAILABLE COPY**

5           METHODS FOR PLANARIZATION OF GROUP VIII METAL-  
CONTAINING SURFACES USING OXIDIZING GASES

Field of the Invention

          The present invention relates to methods for planarization of  
10   Group VIII metal-containing (preferably, platinum-containing) surfaces,  
particularly in the fabrication of semiconductor devices.

Background of the Invention

          Films of metals and metal oxides, particularly the heavier  
15   elements of Group VIII, are becoming important for a variety of electronic and  
electrochemical applications. This is at least because many of the Group VIII  
metal films are generally unreactive, resistant to oxidation or retard the  
diffusion of oxygen, and are good conductors. Oxides of certain of these  
metals also possess these properties, although perhaps to a different extent.

20           Thus, films of Group VIII metals, their alloys, and metal oxides,  
particularly the second and third row metals (e.g., Ru, Os, Rh, Ir, Pd, and Pt)  
have suitable properties for a variety of uses in integrated circuits. For  
example, they can be used in integrated circuits for barrier materials, for  
example. They are particularly suitable for use as barrier layers between the  
25   dielectric material and the silicon substrate in memory devices. Furthermore,  
they are suitable as the plate (i.e., electrode) itself in capacitors.

          Platinum is one of the candidates for use as an electrode for high  
dielectric capacitors. Capacitors are the basic charge storage devices in random  
access memory devices, such as dynamic random access memory (DRAM)  
30   devices, static random access memory (SRAM) devices, and now ferroelectric  
memory (FE RAM) devices. They consist of two conductors, such as parallel  
metal or polysilicon plates, which act as the electrodes (i.e., the storage node  
electrode and the cell plate capacitor electrode), insulated from each other by a

dielectric material (a ferroelectric dielectric material for FE RAMs). Thus, there is a continuing need for methods and materials for the processing of Group VIII metal-containing films, preferably, platinum-containing films.

Many surfaces that result during the formation of Group VIII metal-containing films, particularly in the wafer fabrication of semiconductor devices, do not have uniform height, and therefore, the wafer thickness is also non-uniform. Further, surfaces may have defects such as crystal lattice damage, scratches, roughness, or embedded particles of dirt or dust. For various fabrication processes to be performed, such as lithography and etching, height non-uniformities and defects at the surface of the wafer must be reduced or eliminated. Also, excess material may need to be removed to form a structure with selectivity relative to the underlying substrate. Various planarization techniques are available to provide such reduction and/or elimination. One such planarization technique includes mechanical and/or chemical-mechanical polishing (abbreviated herein as "CMP").

The process of planarization is used to remove material, and preferably achieve a planar surface, over the entire chip and wafer, sometimes referred to as "global planarity." Conventionally, the process of planarization, and particularly CMP, involves the use of a wafer holder that holds a wafer, a polishing pad, and an abrasive slurry that includes a dispersion of a plurality of abrasive particles in a liquid. The abrasive slurry is applied so that it contacts the interface of the wafer and the polishing pad. A table or platen has a polishing pad thereon. The polishing pad is applied to the wafer at a certain pressure to perform the planarization. At least one of the wafer and a polishing pad are set in motion relative to the other. In some planarization processes, the wafer holder may or may not rotate, the table or platen may or may not rotate and/or the platen may be moved in a linear motion as opposed to rotating. There are numerous types of planarization units available which perform the process in different manners. Alternatively, the polishing pad and abrasive slurry may be replaced by a fixed abrasive article that includes a plurality of abrasive particles dispersed within a binder adhered to at least one surface of a backing material.

The planarization of a surface that includes platinum and other Group VIII metals typically involves more mechanical than chemical action during a polishing process because they are relatively chemically inert and/or have relatively few volatile products. Such mechanical polishing uses alumina and silica particles. Unfortunately, mechanical polishing tends to cause the formation of defects (e.g., scratches and particles), both of which can be detected optically, rather than the clean removal of the platinum. Also, many commercially available abrasive slurries do not effectively planarize platinum or other Group VIII metal-containing surfaces either because no material is removed (which results in no change in resistance of the wafer) or the resultant surface has defects therein.

Thus, there is still a need for methods for planarizing an exposed surface of a substrate that includes platinum and/or other Group VIII metals, particularly in the fabrication of semiconductor devices.

#### Summary of the Invention

The present invention provides methods that overcome many of the problems associated with the planarization of a surface that includes platinum and/or another of the Group VIII second or third row metals (i.e., Groups 8, 9, and 10, preferably, Rh, Ru, Ir, Pd, and Pt). Such a surface is referred to herein as a platinum-containing surface, or more generally, a Group VIII metal-containing surface. A "Group VIII metal-containing surface" refers to an exposed region having a Group VIII metal (particularly, platinum) preferably present in an amount of at least about 10 atomic percent, more preferably at least about 20 atomic percent, and most preferably at least about 50 atomic percent, of the composition of the region, which may be provided as a layer, film, coating, etc., to be planarized (e.g., via chemical-mechanical or mechanical planarization or polishing) in accordance with the present invention. The surface preferably includes one or more Group VIII metals in elemental form or an alloy thereof (with each other and/or one or more other metals of the Periodic Table), as well as oxides, nitrides, and silicides thereof. More preferably, the surface includes (and most preferably, consists essentially of)

one or more Group VIII metals in elemental form or an alloy of Group VIII metals only.

The methods of the present invention involve planarizing a surface using a planarization composition that preferably includes a solid or liquid  
5 oxidant (i.e., oxidizer or oxidizing agent) therein (either dispersed or dissolved therein) that has a standard reduction potential of at least about 1.4 versus a standard hydrogen electrode at 25°C.

Preferably, the oxidizing gas is present in the composition in an amount such that the solution is saturated. More preferably, the oxidizing gas is  
10 present in the composition in an amount of no greater than about 10% by weight, and more preferably, in an amount of about 0.1% to about 1% by weight. A particularly preferred group of oxidants includes oxygen, nitrous oxide, air, or combinations thereof.

Herein, as is conventionally understood, "planarizing" or  
15 "planarization" refers to the removal of material from a surface, whether it be a large or small amount of material, either mechanically, chemically, or both. This also includes removing material by polishing. As used herein, "chemical-mechanical polishing" and "CMP" refer to a dual mechanism having both a chemical component and a mechanical component, wherein corrosion chemistry  
20 and fracture mechanics both play a roll in the removal of material, as in wafer polishing.

The planarization composition can optionally include abrasive particles, thereby resulting in an abrasive slurry, and be used in planarization techniques with conventional polishing pads that do not have abrasive particles  
25 embedded therein. Alternatively, the planarization composition without abrasive particles therein can be used with fixed abrasive articles (also referred to as abrasive polishing pads) in place of conventional polishing pads. Such fixed abrasive articles include a plurality of abrasive particles dispersed within a binder adhered to at least one surface of a backing material. Whether in a  
30 fixed abrasive article or in the planarization composition, preferred abrasive particles have a hardness of no greater than about 9 Mohs. If the oxidizing gas is not stable in a composition with abrasive particles (i.e., an abrasive slurry),

they may be provided by separate delivery systems and/or in separate compositions and mixed at the point of use.

In one aspect of the present invention, a planarization method is provided that includes: positioning a Group VIII metal-containing surface of a  
5 substrate (preferably, a semiconductor substrate or substrate assembly such as a wafer) to interface with a polishing pad; supplying a planarization composition in proximity to the interface; and planarizing the Group VIII metal-containing surface. The Group VIII metal is selected from the group consisting of rhodium, iridium, ruthenium, osmium, palladium, platinum, and combinations  
10 thereof. The planarization composition includes an oxidizing gas having a standard reduction potential of at least about 1.4 versus a standard hydrogen electrode at 25°C.

In another aspect of the invention, a planarization method includes: positioning a Group VIII metal-containing surface of a substrate to  
15 interface with a polishing surface, wherein the Group VIII metal is selected from the group consisting of rhodium, iridium, ruthenium, osmium, palladium, platinum, and combinations thereof; supplying a planarization composition in proximity to the interface; and planarizing the Group VIII metal-containing surface; wherein the planarization composition comprises an oxidizing gas  
20 selected from the group consisting of oxygen, air, chlorine, nitrous oxide, nitric oxide, sulfur trioxide, an interhalogen, and combinations thereof.

In yet another aspect of the invention, a planarization method includes: positioning a Group VIII metal-containing surface of a substrate to interface with a polishing surface, wherein the Group VIII metal is selected  
25 from the group consisting of rhodium, iridium, ruthenium, osmium, palladium, platinum, and combinations thereof; supplying a planarization composition in proximity to the interface; and planarizing the Group VIII metal-containing surface; wherein the planarization composition comprises an oxidizing gas having a standard reduction potential of at least about 1.4 versus a standard  
30 hydrogen electrode at 25°C, wherein the oxidizing gas is present in the composition in an amount of no greater than about 10% by weight.

Yet another aspect includes a planarization method that includes:

providing a semiconductor substrate or substrate assembly including at least one region of a platinum-containing surface; providing a polishing surface; providing a planarization composition at an interface between the at least one region of platinum-containing surface and the polishing surface; and planarizing  
5 the at least one region of platinum-containing surface; wherein the planarization composition comprises an oxidizing gas having a standard reduction potential of at least about 1.4 versus a standard hydrogen electrode at 25°C.

In another aspect there is provided a planarization method for use in forming a capacitor or barrier layer that includes: providing a wafer having a  
10 patterned dielectric layer formed thereon and a Group VIII metal-containing layer formed over the patterned dielectric layer, wherein the Group VIII metal is selected from the group consisting of rhodium, iridium, ruthenium, osmium, palladium, platinum, and combinations thereof; positioning a first portion of a polishing surface for contact with the Group VIII metal-containing layer;  
15 providing a planarization composition in proximity to the contact between the polishing surface and the Group VIII metal-containing layer; and planarizing the Group VIII metal-containing layer; wherein the planarization composition comprises an oxidizing gas having a standard reduction potential of at least about 1.4 versus a standard hydrogen electrode at 25°C.

20 As used herein, "semiconductor substrate or substrate assembly" refers to a semiconductor substrate such as a base semiconductor layer or a semiconductor substrate having one or more layers, structures, or regions formed thereon. A base semiconductor layer is typically the lowest layer of silicon material on a wafer or a silicon layer deposited on another material, such  
25 as silicon on sapphire. When reference is made to a substrate assembly, various process steps may have been previously used to form or define regions, junctions, various structures or features, and openings such as capacitor plates or barriers for capacitors.

30

#### Brief Description of the Figures

Figure 1A and 1B are cross-sectional illustrations of one portion

of a wafer before and after a planarization process has been performed in accordance with the present invention.

Figures 2A and 2B are cross-sectional illustrations of one portion of a wafer before and after a planarization process has been performed in  
5 accordance with the present invention.

#### Description of the Preferred Embodiments

The present invention provides methods of planarization of a surface that includes platinum and/or one or more of the other Group VIII  
10 metals. The Group VIII metals are also referred to as the Group VIIB elements or transition metals of Groups 8, 9, and 10 of the Periodic Table. The second and third row Group VIIB metals include Rh, Ru, Ir, Pd, Pt, and Os. Preferably, surfaces that include Rh, Ru, Ir, Pd, and/or Pt can be planarized according to methods of the present invention. Such a surface is referred to  
15 herein as a Group VIII metal-containing surface (this refers to those containing second and/or third row transition metals).

Preferably, a "Group VIII metal-containing surface" refers to an exposed region having a Group VIII metal (particularly, platinum) present in an amount of at least about 10 atomic percent, more preferably at least about 20  
20 atomic percent, and more preferably at least about 50 atomic percent, of the composition of the region, which may be provided as a layer, film, coating, etc., to be planarized (e.g., via chemical-mechanical or mechanical planarization or polishing) in accordance with the present invention.

The planarization of such surfaces, particularly a surface that  
25 includes platinum, typically involves mechanical methods with relatively hard particles such as alumina ( $\text{Al}_2\text{O}_3$ ) and/or silica ( $\text{SiO}_2$ ) particles, which by themselves can cause severe smearing, slow removal rates, and defects, rather than the clean removal of the material. Use of a planarization composition that includes an oxidizing gas either in combination with a plurality of abrasive  
30 particles in the composition or with a fixed abrasive article reduces, and often eliminates, the problem of defect formation, smearing, and often results in increased selectivity and removal rates.



Significantly, the methods of the present invention are particularly advantageous in removing platinum-containing or other second and third row Group VIII metal-containing materials (e.g., metals, alloys, oxides) from a surface in preference to materials containing other metals. This is important in selectively removing material from platinum-containing or other second and third row Group VIII metal-containing layers without removing, for example, significant amounts of underlying layers, such as oxide layers and nitride layers (e.g., TEOS or BPSG layers). Preferably, the selectivity for removal of material from a second and third row Group VIII metal-containing surface relative to materials containing other metals (e.g., BPSG or TEOS) is at least about 10:1, and more preferably, within a range of about 20:1 to about 100:1, depending on the chemistry and process conditions.

The planarization composition can be used in slurry planarization (i.e., in a conventional planarization process in which the planarization composition includes the abrasive particles with a polishing pad that does not include abrasive particles) or in fixed abrasive planarization. Thus, as used herein, a "polishing surface" refers to a polishing pad or a fixed abrasive article. Preferably, slurry planarization is used in the methods of the present invention. Preferably, when present in the planarization composition, the composition includes the abrasive particles in an amount of about 1% by weight to about 30% by weight, and more preferably, about 1% by weight to about 15% by weight, based on the total weight of the composition.

Typically, lower amounts of abrasive particles provide better selectivity of the Group VIII metal-containing surface relative to an oxide layer such as BPSG. Generally, however, the optimum level of selectivity for a particular metal is obtained by balancing the type and amount of abrasive particles, the type and amount of oxidizing gas, and the pH of the composition.

A wide variety of abrasive particles can be used either in an abrasive slurry or in a fixed abrasive article. Typically, such abrasive particles range in particle size (i.e., the largest dimension of the particle) on average from about 10 nanometers (nm) to about 5000 nm, and more often about 30 nm to about 1000 nm. For preferred embodiments, suitable abrasive particles have an

average particle size of about 100 nm to about 300 nm.

Examples of suitable abrasive particles include, but are not limited to, alumina ( $\text{Al}_2\text{O}_3$ ), silica ( $\text{SiO}_2$ ), ceria ( $\text{CeO}_2$ ), titania ( $\text{TiO}_2$ ), zirconia ( $\text{ZrO}_2$ ), manganese dioxide ( $\text{MnO}_2$ ), and tantalum dioxide ( $\text{TaO}_2$ ). Preferred abrasive  
5 particles include alumina ( $\text{Al}_2\text{O}_3$ ), silica ( $\text{SiO}_2$ ), ceria ( $\text{CeO}_2$ ), titania ( $\text{TiO}_2$ ), and zirconia ( $\text{ZrO}_2$ ). Various combinations of abrasive particles can be used if desired.

Preferably, for certain embodiments, abrasive particles include those that have a hardness of no greater than about 9 Mohs, and more preferably  
10 no less than about 6 Mohs. These include, for example, ceria ( $\text{CeO}_2$ ), which has a hardness of about 6 Mohs, alumina ( $\text{Al}_2\text{O}_3$ ), which has a hardness of about 9 Mohs, and silica ( $\text{SiO}_2$ ), which has a hardness of about 7.

In certain methods in accordance with the present invention, preferably, a majority of the plurality of abrasive particles (either in an abrasive  
15 slurry or in a fixed abrasive article) are  $\text{CeO}_2$  particles. This typically results in reduced formation of defects. In certain other methods in accordance with the present invention, preferably, a majority of the plurality of abrasive particles (either in an abrasive slurry or in a fixed abrasive article) have a hardness of about 8 Mohs to about 9 Mohs. This typically results in increased removal rates.

20 The planarization composition includes a gaseous oxidizing agent (i.e., oxidizer or oxidant) having a standard reduction potential of at least about 1.4 versus standard hydrogen electrode at 25°C. The oxidizing agent is a gas at room temperature. It is dissolved in the planarization composition, which typically includes water as the liquid medium.

25 Examples of suitable oxidizing gases include oxygen, ozone, air, chlorine, nitrous oxide, nitric oxide, sulfur trioxide, and an interhalogen (e.g.  $\text{ClF}_3$ ). Various combinations of such oxidizing gases can be used in the methods of the present invention. A preferred group of oxidizing agents include oxygen, air, chlorine, nitrous oxide, nitric oxide, sulfur trioxide, and an  
30 interhalogen. A more preferred group of oxidizing agents include oxygen, nitrous oxide, and air. A most preferred group of oxidizing gases include oxygen and air.

Preferably, the oxidizing gas is present in the composition in an amount such that the solution is saturated. More preferably, the oxidizing gas is present in the composition in an amount of no greater than about 10% by weight, and more preferably, in an amount of about 0.1% to about 1% by weight, based on the total weight of the composition. For certain embodiments, however, higher amounts of the oxidant can be used if desired.

For various desired effects, a planarization composition can optionally and preferably include a complexing agent as described in Applicants' Assignee's copending U.S. Patent Application Serial Number 10/028,040, filed on December 21, 2001 entitled METHODS FOR PLANARIZATION OF GROUP VIII METAL-CONTAINING SURFACES USING COMPLEXING AGENTS, to aid in the planarization. Such complexing agents are chosen such that their effectivity is not destroyed by the oxidizing gas. Other additives can be included as well for desired effects. These include, but are not limited to, a surfactant (e.g., polyethylene glycol, polyoxy ethylene ether, or polypropylene glycol) to enhance wettability and reduce friction, a thickener (e.g., CARBOPOL) to achieve a desired viscosity, a buffering agent (e.g.,  $H_2SO_4$ ,  $NH_4OH$ , acetate, and acetic acid) to achieve a desired pH, etc. Preferably, the composition is an aqueous solution of these components. More preferably, the aqueous planarization composition has an acidic pH.

For certain embodiments, the planarization composition includes a plurality of abrasive particles. For other embodiments, the planarization composition is essentially free of abrasive particles when supplied to the interface of the fixed abrasive article and the workpiece surface. However, in these latter embodiments, it is contemplated that planarization is accomplished by one or both of the fixed abrasive article and/or abrasive particles that may be removed from the fixed abrasive article at the fixed abrasive/surface interface in combination with the planarization composition. In any event, abrasive particles are typically not present in the composition as initially applied, i.e., they are not supplied from a source external to the polishing interface.

Preferably, a method in accordance with the present invention is

conducted at atmospheric pressure and at a temperature of about 40°F (about 4°C) to about 115°F (about 46°C), and more preferably at a temperature of about 75°F (24°C) to about 115°F (46°C). In many instances, however, it would be desirable to maintain a temperature at or below ambient temperature during planarization of Group VIII metal with a fixed abrasive article. This is seldom practical in slurry planarization (i.e., in a conventional planarization process in which the planarization composition includes the abrasive particles) where a lower slurry temperature likely results in poor dispersion of abrasive particles in the slurry composition during planarization. Accordingly, elevated temperatures are typically utilized during slurry planarization, although too high a temperature could result in too low a concentration of oxidizing gas in the planarization composition.

Various planarization assemblies or units for performing methods of the invention are readily available and are clearly contemplated by the scope of the present invention as described in the accompanying claims. Such planarization assemblies can create an interface between a polishing pad or a fixed abrasive article and the substrate surface (e.g., wafer surface) in various manners, e.g., rotation, movement, pressure, etc., to achieve planarization. A planarization composition is typically introduced at or near the interface, by a variety of methods such as by dripping, spraying, or other dispensing means, or by presoaking a polishing pad, although other locations and methods of introduction can be used.

In a typical planarizing machine, a polishing pad is fixed on a platen or table, a carrier assembly that includes a substrate holder to support the substrate (e.g., wafer) typically using suction, and a drive assembly to rotate and/or reciprocate the platen and/or a drive assembly to rotate and/or translate the substrate holder during planarization. Thus, conventional planarizing machines rotate the carrier assembly, the polishing pad, or both the carrier assembly and the polishing pad. In general, the planarizing machines are used to produce a planarization reaction product at the surface of a substrate whose hardness is less than the hardness of the abrasive particles and whose adhesion to the substrate is less than the original surface material; and to remove the

reaction produce using the abrasive particles.

Typically, the polishing pads, with or without abrasive particles embedded therein, are disk-shaped and rotatable about a fixed plane and axis at constant or variable speeds. Typically, the speed of rotation ranges from about  
5 2 revolutions per minute (rpm) to about 200 rpm.

Typically, a polishing pad is presoaked and continually rewet with the planarization composition. If the polishing pad does not include abrasive particles embedded therein, the planarization composition includes abrasive particles, which is then referred to as an abrasive slurry. The planarization  
10 composition may be applied to the interface between a polishing pad and a substrate surface using a variety of techniques. For example, the component parts of the composition may be applied separately and mixed at the interface or immediately before contacting the interface. The planarization composition can be applied by pumping it through the pad. Alternatively, it can be applied at the  
15 leading edge of the pad, although this may not provide uniform distribution of the planarization composition across the surface being planarized, which is desirable.

The polishing pad can be any of a wide variety of conventional polishing pads that are used with abrasive slurries. They can be made from a  
20 material such as polyurethane, polyester, acrylic, acrylic ester copolymers, polytetrafluoroethylene, polypropylene, polyethylene, cellulose, cellulose esters, polyamides, polyimides, polysiloxane, polycarbonates, epoxides, phenolic resins, etc. They include, for example, a polyurethane-based foam material, wherein the foam cell walls of the pad aid in removal of reaction products at the  
25 wafer surface and the pores within the pad assist in supplying slurry to the pad/wafer interface. They can include convex or concave features, which can be formed by embossing a surface pattern. For example, a polishing pad can have continuous grooves in concentric ellipses in the surface of the pad for more uniform slurry delivery and more effective debris removal. Commercially  
30 available polishing pads can be obtained under the trade designations "URII," "Sycamore," and "Polytex" from Rodel, Phoenix, AZ. Examples of polishing pads are also disclosed in U.S. Pat. No. 6,039,633 (Chopra).

In general, a fixed abrasive article includes a plurality of abrasive particles dispersed within a binder that forms a three-dimensional fixed abrasive element that is adhered to one surface of a backing material. They are described, for example, in U.S. Patent No. 5,692,950 (Rutherford, et al.) and  
5 International Patent Publication WO 98/06541. Commercially available fixed abrasive articles can be obtained from Tokyo Sumitsu Kageki and Ebera Corporation, both of Japan, and Minnesota Mining and Manufacturing Company (3M Company) of St. Paul, MN. An example of a preferred fixed abrasive article is a ceria-based pad commercially available from 3M Company  
10 under the trade designation "SWR 159." Such fixed abrasive articles can be used with a planarization composition as described herein with or without abrasive particles in the planarization composition.

It is highly desirable to have a high polishing rate (i.e., the rate at which material is removed from the substrate) to reduce the duration of each  
15 planarizing cycle, the polishing rate is preferably uniform across the substrate to produce a uniformly planar surface. Preferably, the polishing rate is controlled to provide accurate, reproducible results. Also, preferably, the planarization process is carried out in one cycle (i.e., one step). That is, for the removal of any material from a particular surface, there is only one planarization cycle  
20 without any intervening rinse cycles. This planarization process is then typically followed by a post-planarization clean process in which abrasive particles are not used.

The figures provide further information about the methods of the invention. Figure 1A illustrates one portion of a wafer 10 prior to planarization  
25 in accordance with the present invention having features that are filled with the material to be removed through planarization. The wafer portion 10 includes a substrate assembly 12 having junctions 16 formed thereon. A capacitor and/or barrier layer material 19 is then formed over the substrate assembly 12 and the junctions 16. The capacitor and/or barrier layer material 19 may be any  
30 conductive material such as platinum or any other suitable conductive second or third row Group VIII metal-containing capacitor and/or barrier material. Generally, as shown in Figure 1A, the nonplanar upper surface 13 of capacitor

and/or barrier layer 19 is subjected to planarization or other processing in accordance with the present invention. The resulting wafer 10, which is shown in Figure 1B, includes an upper surface 17 planarized such that the thickness of the wafer 10 is substantially uniform across the entire wafer 10 so that the wafer  
5 now includes a capacitor and/or barrier structure layer 14.

Figure 2A illustrates one portion of a wafer 20 prior to planarization in accordance with the present invention having features that have a conformal layer of the material to be removed through planarization. The wafer portion 20 includes a substrate assembly 22 having a patterned dielectric  
10 layer 26 formed thereon. Such a patterned dielectric layer 26 can be used in a variety of structures, particularly a capacitor structure. The patterned dielectric layer 26 can be formed of any material that provides electrical isolation between metal regions (e.g., silicon dioxide, silicon nitride, or BPSG). An electrode layer 29 is then formed over the substrate assembly 22 and the  
15 patterned dielectric layer 26. The electrode layer 29 may be platinum or any other suitable conductive second or third row Group VIIIB or Group IB metal-containing material. Generally, as shown in Figure 2A, the nonplanar upper surface 23 of electrode layer 29 is subjected to planarization or other processing in accordance with the present invention. The resulting wafer 20, as shown in  
20 Figure 2B, includes an upper surface 27 planarized such that the thickness of the wafer 20 is substantially uniform across the entire wafer 20 so that the wafer now includes electrically conducting regions 24 isolated within the patterned dielectric material 26 forming a capacitor structure. If desired, prior to planarization, the conformal layer 29 and openings 24 can be covered with a  
25 photoresist or other material that is removed after the planarization so the abrasive does not fall into the openings 24.

These figures are shown only to illustrate a surface having nonuniformities, such as height differences, in the fabrication of semiconductor devices. The present invention is not limited to use with nonplanar surfaces,  
30 such as that shown in figures. The present invention is also beneficial for use with substantially planar surfaces. For example, the methods in accordance with the present invention is beneficial during the whole planarization process,

even at the end of the process when the surface being planarized is in a substantially planar state.

The following example is offered to further illustrate the various specific and preferred embodiments and techniques. It should be understood, however, that many variations and modifications may be made while remaining within the scope of the present invention.

#### Example

A blanket platinum wafer is used as a test sample. A slurry is prepared by diluting three liters of Rodel Granite Part A slurry with three liters of water. To that mixture 10 mL of concentrated acetic acid is added. The mixture is stirred for thirty minutes. For the polish, a conventional, rotary polisher such as AMAT MIRRA is used with a Rodel URII pad. The tool is modified to allow the addition of oxygen into the slurry shortly before entering the pad. The gas is added with a flow of 10 sccm. The polish is performed with a down force of 4.5 lbs, table speed of 55 rpm and head speed of 50 rpm. Slurry flow is set to 150 mL/min. After polishing the wafer is cleaned with conventional scrubbing.

The foregoing detailed description and example have been given for clarity of understanding only. No unnecessary limitations are to be understood therefrom. The invention is not limited to the exact details shown and described, for variations obvious to one skilled in the art will be included within the invention defined by the claims. For example, while the description above focused on planarization of semiconductor-based substrates, the compositions and methods of the invention are also applicable to, for example, polishing glasses and contact lenses, as one of many other possible applications. The complete disclosures of all patents, patent documents, and publications listed herein are incorporated by reference, as if each were individually incorporated by reference.



## What Is Claimed Is:

1. A planarization method comprising:
  - positioning a Group VIII metal-containing surface of a substrate to  
5 interface with a polishing surface, wherein the Group VIII metal is  
selected from the group consisting of rhodium, iridium, ruthenium,  
osmium, palladium, platinum, and combinations thereof;  
supplying a planarization composition in proximity to the  
interface;  
10 and  
planarizing the Group VIII metal-containing surface;  
wherein the planarization composition comprises an oxidizing gas  
having a standard reduction potential of at least about 1.4 versus a  
standard hydrogen electrode at 25°C.
- 15 2. The method of claim 1 wherein the Group VIII metal-containing  
surface of the substrate comprises a Group VIII metal in elemental form  
or an alloy thereof.
- 20 3. The method of claim 2 wherein the Group VIII metal-containing surface  
comprises elemental platinum, rhodium, iridium, ruthenium, or a  
combination thereof.
4. The method of claim 3 wherein the Group VIII metal-containing surface  
25 comprises elemental platinum.
5. The method of claim 1 wherein the Group VIII metal is present in an  
amount of about 10 atomic percent or more.
- 30 6. The method of claim 1 wherein the substrate is a semiconductor  
substrate or substrate assembly.

7. The method of claim 1 wherein the polishing surface comprises a polishing pad and the planarization composition comprises a plurality of abrasive particles.
- 5 8. The method of claim 1 wherein the planarization composition comprises a plurality of abrasive particles having a hardness of no greater than about 9 Mohs.
9. The method of claim 8 wherein the plurality of abrasive particles  
10 comprise  $\text{CeO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ , and mixtures thereof.
10. The method of claim 1 which is carried out in one step.
11. The method of claim 1 wherein the oxidizing gas is selected from the  
15 group consisting of oxygen, ozone, air, chlorine, nitrous oxide, nitric oxide, sulfur trioxide, an interhalogen, and combinations thereof.
12. The method of claim 11 wherein the oxidizing gas is selected from the  
20 group consisting of oxygen, air, and combinations thereof.
13. The method of claim 12 wherein the oxidizing gas is oxygen.
14. The method of claim 1 wherein planarizing is carried out using a fixed  
25 abrasive article.
15. A planarization method comprising:  
positioning a Group VIII metal-containing surface of a substrate to  
interface with a polishing surface, wherein the Group VIII metal is  
selected from the group consisting of rhodium, iridium, ruthenium,  
30 osmium, palladium, platinum, and combinations thereof;  
supplying a planarization composition in proximity to the  
interface;

- and  
planarizing the Group VIII metal-containing surface;  
wherein the planarization composition comprises an oxidizing gas  
selected from the group consisting of oxygen, air, chlorine, nitrous  
oxide, nitric oxide, sulfur trioxide, an interhalogen, and combinations  
thereof.
16. A planarization method comprising:  
positioning a Group VIII metal-containing surface of a substrate to  
interface with a polishing surface, wherein the Group VIII metal is  
selected from the group consisting of rhodium, iridium, ruthenium,  
osmium, palladium, platinum, and combinations thereof;  
supplying a planarization composition in proximity to the  
interface;  
and  
planarizing the Group VIII metal-containing surface;  
wherein the planarization composition comprises an oxidizing gas  
having a standard reduction potential of at least about 1.4 versus a  
standard hydrogen electrode at 25°C, wherein the oxidizing gas is  
present in the composition in an amount of no greater than about 10%  
by weight.
17. A planarization method comprising:  
providing a semiconductor substrate or substrate assembly  
including at least one region of a platinum-containing surface;  
providing a polishing surface;  
providing a planarization composition at an interface between the  
at least one region of platinum-containing surface and the polishing  
surface; and  
planarizing the at least one region of platinum-containing surface;

wherein the planarization composition comprises an oxidizing gas having a standard reduction potential of at least about 1.4 versus a standard hydrogen electrode at 25°C.

- 5    18.    The method of claim 17 wherein the platinum is present in an amount of about 10 atomic percent or more.
19.    The method of claim 17 wherein the platinum-containing surface comprises elemental platinum.
- 10    20.    The method of claim 17 wherein the planarization composition comprises a plurality of abrasive particles selected from the group consisting of  $\text{CeO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ , and mixtures thereof.
- 15    21.    The method of claim 17 wherein the platinum-containing surface comprises a platinum alloy.
22.    The method of claim 17 wherein the semiconductor substrate or substrate assembly is a silicon wafer.
- 20    23.    The method of claim 17 wherein the oxidizing gas is selected from the group consisting of oxygen, nitrous oxide, air, or combinations thereof.
24.    The method of claim 23 wherein the oxidizing gas is selected from the group consisting of oxygen, air, or combinations thereof.
- 25    25.    The method of claim 24 wherein the oxidizing gas is selected from the group consisting of oxygen.
- 30    26.    A planarization method for use in forming a capacitor or barrier layer:  
         providing a wafer having a patterned dielectric layer formed thereon and a Group VIII metal-containing layer formed over the

patterned dielectric layer, wherein the Group VIII metal is selected from the group consisting of rhodium, iridium, ruthenium, osmium, palladium, platinum, and combinations thereof;

5       positioning a first portion of a polishing surface for contact with the Group VIII metal-containing layer;

      providing a planarization composition in proximity to the contact between the polishing surface and the Group VIII metal-containing layer;

10       and  
      planarizing the Group VIII metal-containing layer;

      wherein the planarization composition comprises an oxidizing gas having a standard reduction potential of at least about 1.4 versus a standard hydrogen electrode at 25°C.

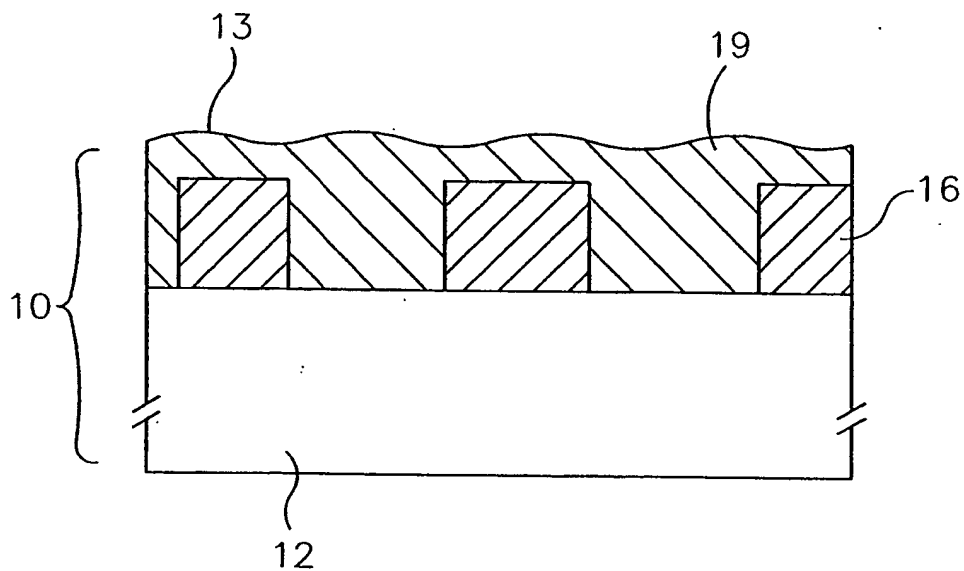
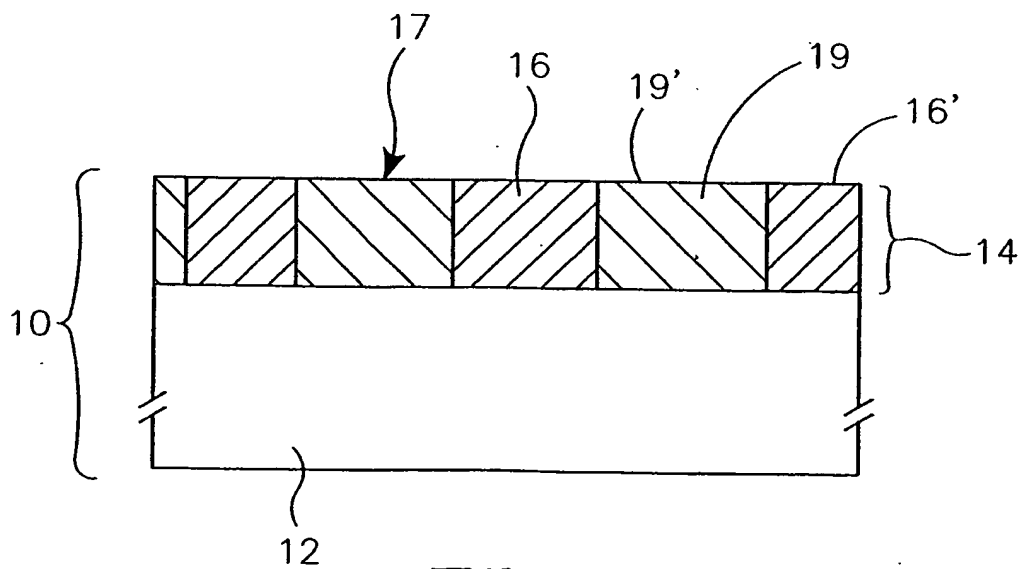
15

20

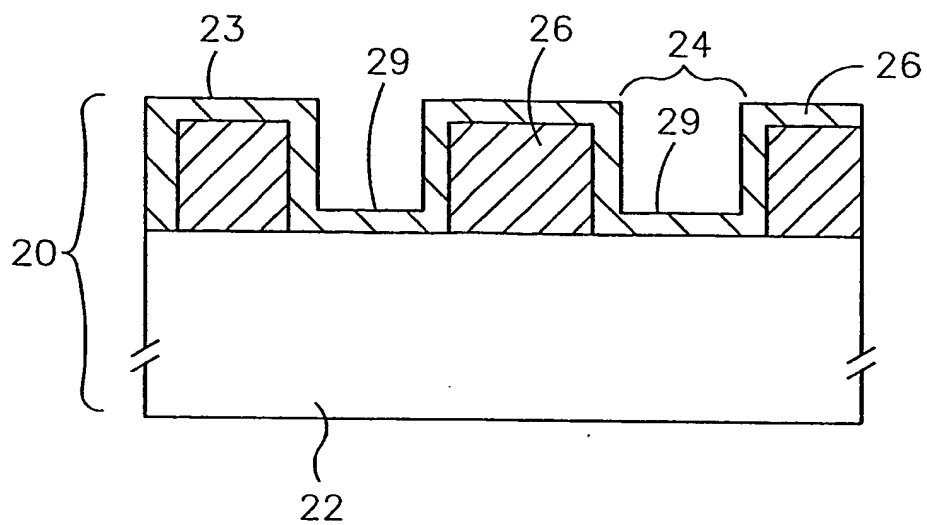
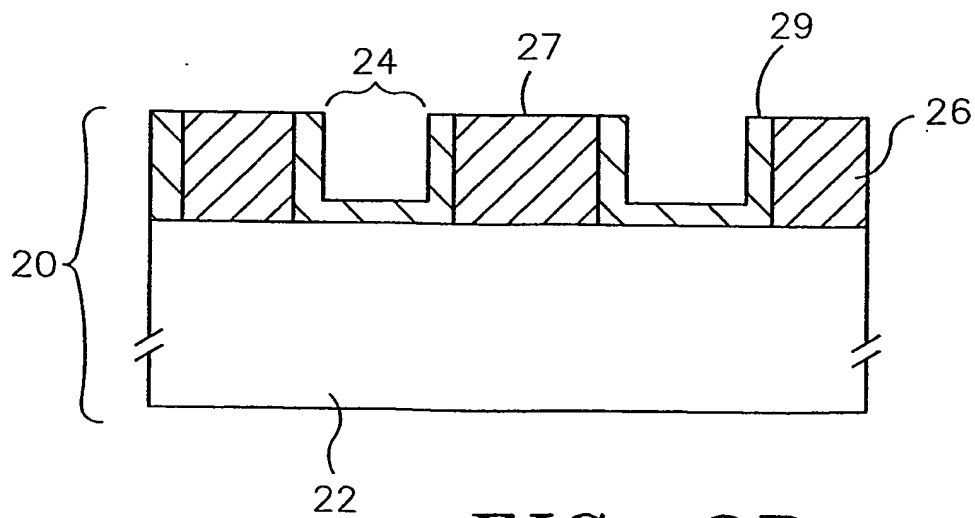
25

30

1/2

*FIG. 1A**FIG. 1B*

2/2

*FIG. 2A**FIG. 2B*

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
24 July 2003 (24.07.2003)

PCT

(10) International Publication Number  
**WO 03/060980 A3**

(51) International Patent Classification<sup>7</sup>: **H01L 21/321**

(21) International Application Number: **PCT/US02/40407**

(22) International Filing Date:  
17 December 2002 (17.12.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
10/032,357 21 December 2001 (21.12.2001) US

(71) Applicant: **MICRON TECHNOLOGY, INC.** [US/US];  
8000 South Federal Way, Boise, ID 83704-0006 (US).

(72) Inventors: **UHLENBROCK, Stefan**; 11336 W. Divide  
Pass Dr., Boise, ID 83709 (US). **WESTMORELAND,  
Donald, L.**; 10258 West Alliance Street, Boise, ID 83704  
(US).

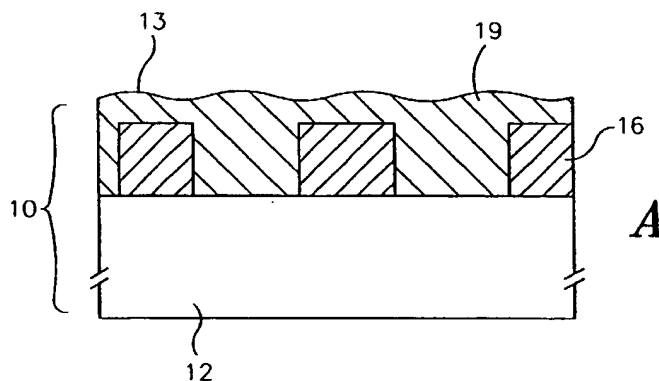
(74) Agent: **MUETING, Ann, M.**; Mueeting, Raasch & Geb-  
hardt, P.A., P.O. Box 581415, Minneapolis, MN 55458-  
1415 (US).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,  
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,  
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,  
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,  
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,  
MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG,  
SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VN, YU,  
ZA, ZM, ZW.

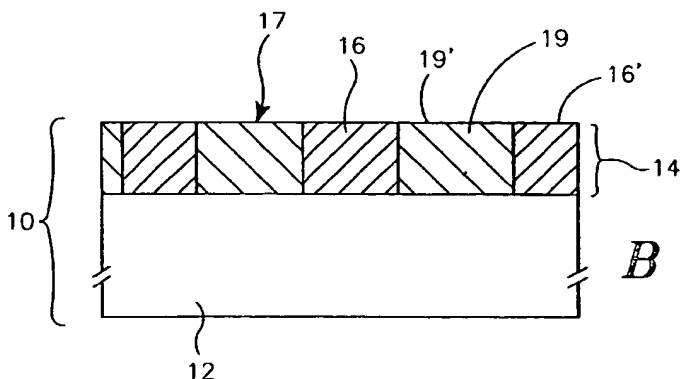
(84) Designated States (*regional*): ARIPO patent (GH, GM,  
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),  
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),  
European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE,  
ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SI, SK,  
TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ,  
GW, ML, MR, NE, SN, TD, TG).

[Continued on next page]

(54) Title: METHODS FOR PLANARIZATION OF GROUP VIII METAL-CONTAINING SURFACES USING OXIDIZING GASES



(57) Abstract: A planarization method includes providing a second and/or third Group VIII metal-containing surface (preferably, a platinum-containing surface) and positioning it for contact with a polishing surface in the presence of a planarization composition that includes an oxidizing gas.



WO 03/060980 A3





**Published:**

— with international search report

**(88) Date of publication of the international search report:**

13 November 2003

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

## INTERNATIONAL SEARCH REPORT

 International Application No  
 PCT/US 02/40407

 A. CLASSIFICATION OF SUBJECT MATTER  
 IPC 7 H01L21/321

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 156 091 A (SIEMENS AG ;INFINEON TECHNOLOGIES AG (DE)) 21 November 2001 (2001-11-21)	1-7, 10-13, 15-19, 21-26
Y	paragraph '0010! - paragraph '0043!; figure 1; example 4 ---	8,9,20
Y	EP 1 111 083 A (INFINEON TECHNOLOGIES AG) 27 June 2001 (2001-06-27)	8,9,20
A	the whole document ---	
X	WO 00 77107 A (UNGER EUGEN ;BEITEL GERHARD (DE); SAENGER ANNETTE (DE); INFINEON T) 21 December 2000 (2000-12-21) the whole document --- -/--	1-7, 10-15

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*Z\* document member of the same patent family

Date of the actual completion of the international search

14 August 2003

Date of mailing of the international search report

22/08/2003

 Name and mailing address of the ISA  
 European Patent Office, P.B. 5818 Patentlaan 2  
 NL - 2280 HV Rijswijk  
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
 Fax: (+31-70) 340-3016

Authorized officer

Hedouin, M

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 02/40407

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 2000, no. 10, 17 November 2000 (2000-11-17) & JP 2000 200782 A (HITACHI LTD), 18 July 2000 (2000-07-18) abstract -----	
A	US 6 110 830 A (MC TEER ALLEN ET AL) 29 August 2000 (2000-08-29) -----	
A	US 6 278 153 B1 (MATSUI KOJI ET AL) 21 August 2001 (2001-08-21) abstract; figures 3-16H -----	

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 02/40407

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 1156091	A	21-11-2001	DE 10024874 A1	29-11-2001
			CN 1324906 A	05-12-2001
			EP 1156091 A1	21-11-2001
			JP 2002033298 A	31-01-2002
			US 2002017063 A1	14-02-2002
EP 1111083	A	27-06-2001	DE 19959711 A1	21-06-2001
			EP 1111083 A2	27-06-2001
			TW 498400 B	11-08-2002
			US 2002008265 A1	24-01-2002
WO 0077107	A	21-12-2000	DE 19927286 A1	18-01-2001
			WO 0077107 A1	21-12-2000
			US 2002081853 A1	27-06-2002
JP 2000200782	A	18-07-2000	US 2002070194 A1	13-06-2002
US 6110830	A	29-08-2000	US 6277746 B1	21-08-2001
US 6278153	B1	21-08-2001	JP 3214460 B2	02-10-2001
			JP 2000124606 A	28-04-2000
			JP 3362776 B2	07-01-2003
			JP 2000223362 A	11-08-2000
			US 2002020836 A1	21-02-2002

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☒ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**